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(54) Title: THERMALLY STABLE POLYESTERS FORMED UTILIZING ANTIMONY COMPOUNDS AS CATALYSTS

(57) Abstract

This invention relates to a thermally stable polyester, comprising: a polyester resin prepared by adding a dicarboxylic acid to a glycol compound, said dicarboxylic acid selected from the group consisting of aliphatic dicarboxylic acids having a total of from 3 to 16 carbon atoms, alicyclic dicarboxylic acids having 7 to 12 carbon atoms, aromatic dicarboxylic acids containing a total of from 8 to 16 carbon atoms, and combinations thereof, and wherein said glycol is selected from the group consisting of glycols having from 2 to 12 carbon atoms, glycol ethers having from 4 to 12 carbon atoms, and combinations thereof, said polyester resin having been prepared in the presence of a catalyst system consisting essentially of one or more antimony compounds which is not reacted with α -hydroxy carboxylic acids, α,β -dicarboxylic acids or derivatives thereof.

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THERMALLY STABLE POLYESTERS FORMED UTILIZING
ANTIMONY COMPOUNDS AS CATALYSTS

Field of the Invention

5 This invention concerns thermally stable polyester resins prepared in the presence of a catalyst system consisting essentially of an antimony compound without the necessity of stabilizers or other metal catalysts.

10 Background of the Invention

 Traditionally, the synthesis of polyesters requires the use of catalysts to provide a sufficient rate of reaction to be commercially viable. Often, however, the catalysts that encourage the forward polymerization
15 reaction also enhance the rates of degradation reactions. These degradation reactions can result in both an increase in color and a decrease in molecular weight. To minimize these unfavorable side reactions, stabilizing agents such as phosphorus compounds are
20 traditionally added to the reaction mixture. It is believed in the art that such a stabilizer is needed to prepare a material with acceptable color and thermal stability.

 For example, a common commercial catalyst in the
25 synthesis of polyesters is titanium. Titanium is an extremely active catalyst and requires the addition of phosphorus compounds to provide acceptable thermal stability as well as improve the color. Antimony is also known as a catalyst in the synthesis of polyesters.
30 Although antimony is a less active catalyst than titanium, the art teaches the addition of phosphorus compounds to provide acceptable thermal stability as well as to improve the color.

 In the production of commercial polyesters, even
35 when phosphorus is added, the polymer formed is

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United States Patent No. 3,732,182 to Chimura et al. relates to the synthesis of novel antimony compounds that do not undergo an undesirable reduction reaction. This article is not pertinent in that it reacts
5 traditional antimony compounds with α -hydroxycarboxylic acid, $-\alpha, \beta$ -dicarboxylic acid or certain derivatives thereof to formulate allegedly novel antimony compounds.

United States Patent No. 4,499,226 to Massey et al. relates to high clarity, colorless, antimony catalyzed
10 polyesters based on terephthalic acid reacted with polyhydric alcohols. This article also requires a stabilizer to prevent color and degradation side reactions. This article also discloses cobalt as a bluing agent.

15 At present, in order to improve the apparent whiteness of polyester fibers or neutral color characteristics of polyester plastics, toners can be incorporated into the polyester to mask or neutralize the yellow color.

20 Cobalt acetate is one of the most widely used toners in the industry to mask the yellow color of polymers. However, cobalt acetate has a number of noteworthy disadvantages. For example, cobalt acetate toned materials tend to be unstable during storage and
25 are particularly susceptible to temperature and humidity, and tend to undergo an undesirable color shift toward yellow. Further, when high cobalt concentrations are needed to mask the yellow color of some polymers there is a tendency to impart a gray color to the
30 polymer.

Another disadvantage in the use of cobalt acetate is the limitation set by various governmental agencies in the level of cobalt deemed allowable in polyester catalyst systems.

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Summary of the Invention

This invention relates to a thermally stable polyester resin having been prepared in the presence of a catalyst system, consisting essentially of an antimony compound wherein the polyester resin is prepared by adding a dicarboxylic acid to a glycol compound. A thermal stabilizer is not necessary in the preparation of this polyester.

More particularly, this invention relates to a thermally stable polyester, comprising a polyester resin, the polyester resin made by adding a dicarboxylic acid to a glycol compound, the carboxylic acid selected from the group consisting of aliphatic dicarboxylic acids having a total of from 3 to 16 carbon atoms, alicyclic dicarboxylic acids having 7 to 12 carbon atoms, aromatic dicarboxylic acids containing a total of from 8 to 16 carbon atoms, and combinations thereof, and wherein the glycol is selected from the group consisting of glycols having from 2 to 12 carbon atoms, glycol ethers having from 4 to 12 carbon atoms, and combinations thereof, where the polyester resin has been prepared in the presence of a catalyst system consisting essentially of an antimony compound.

Further, this invention relates to a method for imparting good thermal stability to polyesters without the need for stabilizers by employing the catalyst system described above.

This invention even further relates to the use of organic dyes in the polyester compositions and in the methods of the present invention.

This invention provides the advantages of good thermal stability without the need for stabilizers. It also provides this improved thermal stability in combination with good color for the polyesters described.

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1.2 (dL/g) measured at 25°C in a 60/40 ratio by weight of phenol/tetrachloroethane.

The dicarboxylic acid may be selected from the group consisting of aliphatic dicarboxylic acids having a total of from 3 to 16 carbon atoms, alicyclic dicarboxylic acids having 7 to 12 carbon atoms, aromatic dicarboxylic acids containing a total of from 8 to 16 carbon atoms, and combinations thereof. The glycol may be selected from the group consisting of glycols having from 2 to 12 carbon atoms, glycol ethers having from 4 to 12 carbon atoms, and combinations thereof.

The term "aliphatic-dicarboxylic acid" is used to denote straight or branched chain alkanedicarboxylic acids containing 3 to 16 carbons. Typical aliphatic dicarboxylic acid include succinic acid, glutaric acid, adipic acid, sebacic acid, suberic, 2,2,4-trimethyladipic, 1,12-dodecanedioic acid and the like.

The term "alicyclic dicarboxylic acid" is used to denote cycloalkane dicarboxylic acids which contain a total of 7 to 12 carbon atoms preferably 1,2-, 1,3- and 1,4-cyclohexanedicarboxylic acids.

The term "aromatic dicarboxylic acid" is used to denote dicarboxylic acid derivatives of benzene, naphthalene, biphenyl, diphenylether, diphenylsulfone and these substitutes with C₁ - C₄ alkyl or halogen (fluorine, chlorine, bromine or iodine). Typical aromatic dicarboxylic acids, include terephthalic acid, isophthalic acid, phthalic acid, 1,4-naphthalene dicarboxylic acid, 2,6-naphthalenedicarboxylic, 4,4'-biphenyldicarboxylic acid, 2-bromoterephthalic acid, 2,5-dibromoterephthalic acid, tetrachlorophthalic acid and the like. Terephthalic acid, isophthalic acid and 2,6-naphthalenedicarboxylic acid are the preferred aromatic dicarboxylic acids.

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The polyesters may be prepared according to polyester forming conditions well known in the art. For example, a mixture of one or more dicarboxylic acids, preferably aromatic dicarboxylic acids, and one or more diols may be heated in the presence of esterification and/or polyesterification catalysts at temperatures in the range of about 150° to about 300°C, and pressures of atmospheric to about 0.2 mm Hg. Normally, the dicarboxylic acid is esterified with the diol(s) at about 10 to 110 psi, preferably 20 to 60 psi above atmospheric pressure and at a temperature at the lower end of the specified range. Polycondensation then is effected by increasing the temperature and lowering the pressure while excess diol is removed from the mixture.

A preferred temperature range for a polyester condensation is about 225°C to about 300°C.

It is preferred in the cases of polyester containing greater than 5 mole % 1,4-cyclohexanedimethanol, based on the glycol components being present at a total of 100 mole percent, that the polycondensation reaction time is less than 8 hours, preferably less than 4.0 hours and more preferably less than 3.0 hours.

In a preferred embodiment, organic dyes are useful in the polyesters of the invention. Preferred dyes are ones falling within the classes of anthraquinones and anthrapyridones.

When the dyes of the invention are used as toners, this means that it is used in an amount sufficient to improve the apparent whiteness of the polyester. This amount is generally from about 0.1 to 10 ppm. These dyes can also be used in an amount sufficient to impart a substantial amount of color to the polyester. If color is intended to be imparted to the polyester, the dye should be present in an amount greater than 10 ppm.

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R is selected from the group consisting of hydrogen, C₁-C₆ alkyl, halogen, carboxy, and C₁-C₆

5 alkoxy-C(=O)-;

R₁ and R₂ are independently C₁-C₆-alkyl;

R₃ is selected from the group consisting of
 10 hydrogen, halogen, C₁-C₆-alkyl, substituted C₁-C₆ alkyl, hydroxy, C₁-C₆-alkoxy, substituted C₁-C₆-alkoxy, cyano, thiocyanato, C₁-C₆-alkylthio, substituted C₁-C₆-alkylthio, C₁-C₆-alkylsulfonyl, substituted C₁-C₆-alkylsulfonyl, C₁-C₆-alkoxycarbonyl, carboxy, aryloxy, arylthio, aryl-
 15 sulfonyl, and SO₂N(R₄)R₅X when m and/or n are zero;

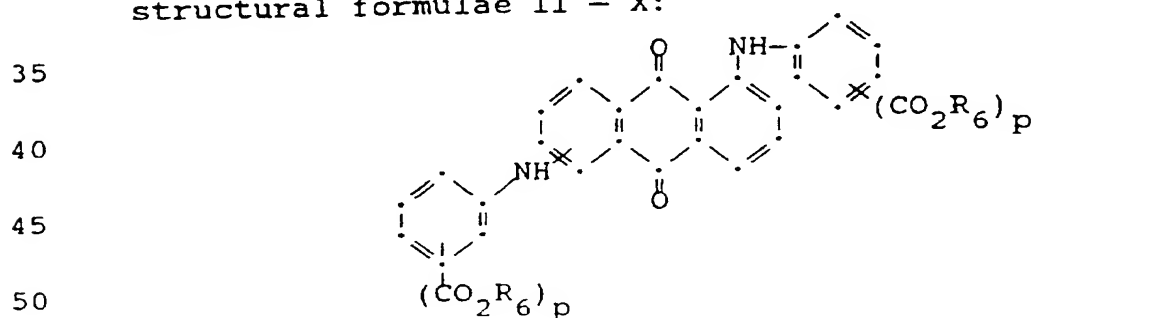
R₄ is selected from the group consisting of hydrogen, C₁-C₆-alkyl, substituted C₁-C₆-alkyl, C₃-C₈-alkenyl, C₃-C₈-alkynyl, C₃-C₇-cycloalkyl and aryl;

R₅ is a linking group selected from the group
 20 consisting of C₁-C₈-alkylene, C₁-C₆-alkylene-Z-C₁-C₆-alkylene, arylene-C₁-C₆-alkylene, arylene-Z-C₁-C₆-alkylene, C₃-C₇-cycloalkylene, C₁-C₆-alkylene-cycloalkylene-C₁-C₆-alkylene, C₁-C₆-alkylene-arylene-C₁-C₆-alkylene, and C₁-C₆-alkylene-Z-arylene-Z-C₁-C₆-alkylene,
 25 wherein Z is selected from -O-, -S- or SO₂;

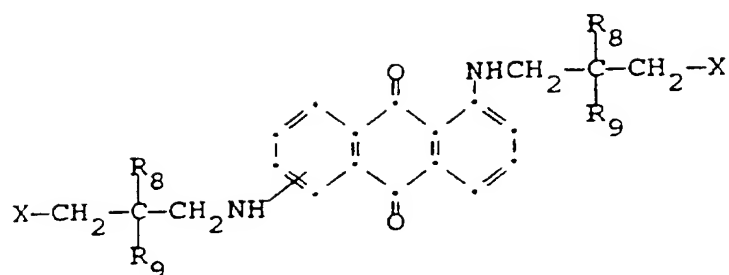
X is hydrogen or a polyester reactive group; and

m and n are independently 0 or 1; with the proviso that at least one polyester reactive group is present.

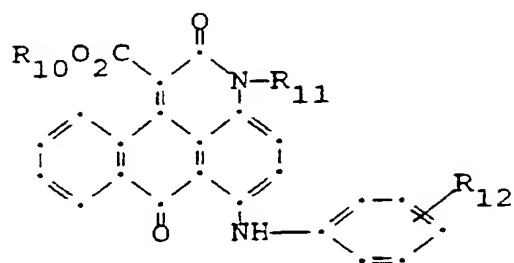
The red components which may be blended with blue
 30 components of formula I above have the following structural formulae II - X:



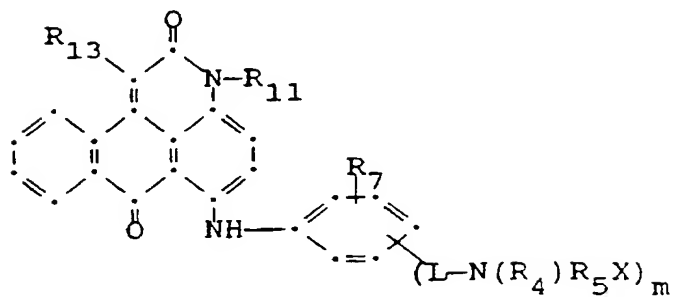
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VI



VII



VIII

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R_{10} is selected from the group consisting of C_1 - C_6 -alkyl, C_3 - C_7 -cycloalkyl or aryl;

R_{11} is selected from the group consisting of hydrogen, C_1 - C_{12} -alkyl, substituted C_1 - C_{12} -alkyl, C_3 - C_7 -cycloalkyl and aryl;

R_{12} is hydrogen or one to three groups selected from the group consisting of C_1 - C_6 -alkyl, substituted C_1 - C_6 -alkyl, C_1 - C_6 -alkoxy, substituted C_1 - C_6 -alkoxy, C_1 - C_6 -alkylthio, substituted C_1 - C_6 -alkylthio, halogen, hydroxy, C_1 - C_6 -alkanoylamino, aroylamino, C_1 - C_6 -alkylsulfonylamino and arylsulfonylamino;

R_{13} and R_{14} are selected from hydrogen, cyano or CO_2R_{10} ;

R_{15} is R_4 or R_5X as previously defined;

L is $-CO-$ or $-SO_2-$; X is as previously defined; m is 0 or 1; p is 1 or 2; with the provisos that R_{13} is hydrogen when m is 0 and at least one polyester reactive group is present.

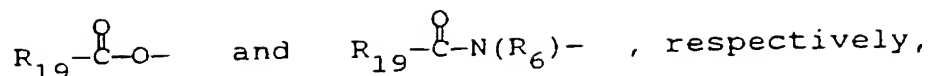
The term "polyester reactive group" is used herein to describe a group which is reactive with at least one of the functional groups from which the polyester is prepared under polyester forming conditions. Examples of the groups which X may represent include hydroxy, carboxy, an ester group, amino, C_1 - C_6 -alkylamino, etc. The ester radicals may be any radical having the formula



wherein R_{16} is selected from the group consisting of C_1 - C_6 -alkyl, substituted C_1 - C_6 -alkyl, C_3 - C_7 -cycloalkyl or aryl. Reactive group X is preferably hydroxy, carboxy, C_1 - C_2 -alkoxycarbonyl or acetoxy.

In the terms "substituted C_1 - C_6 -alkyl", "substituted C_1 - C_{12} -alkyl", "substituted C_1 - C_6 -alkoxy", "substituted C_1 - C_6 -alkylthio", "substituted C_1 - C_6 -

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10 wherein R_{19} is a straight or branched chain C_1 - C_6 -alkyl radical and R_6 is as defined above.

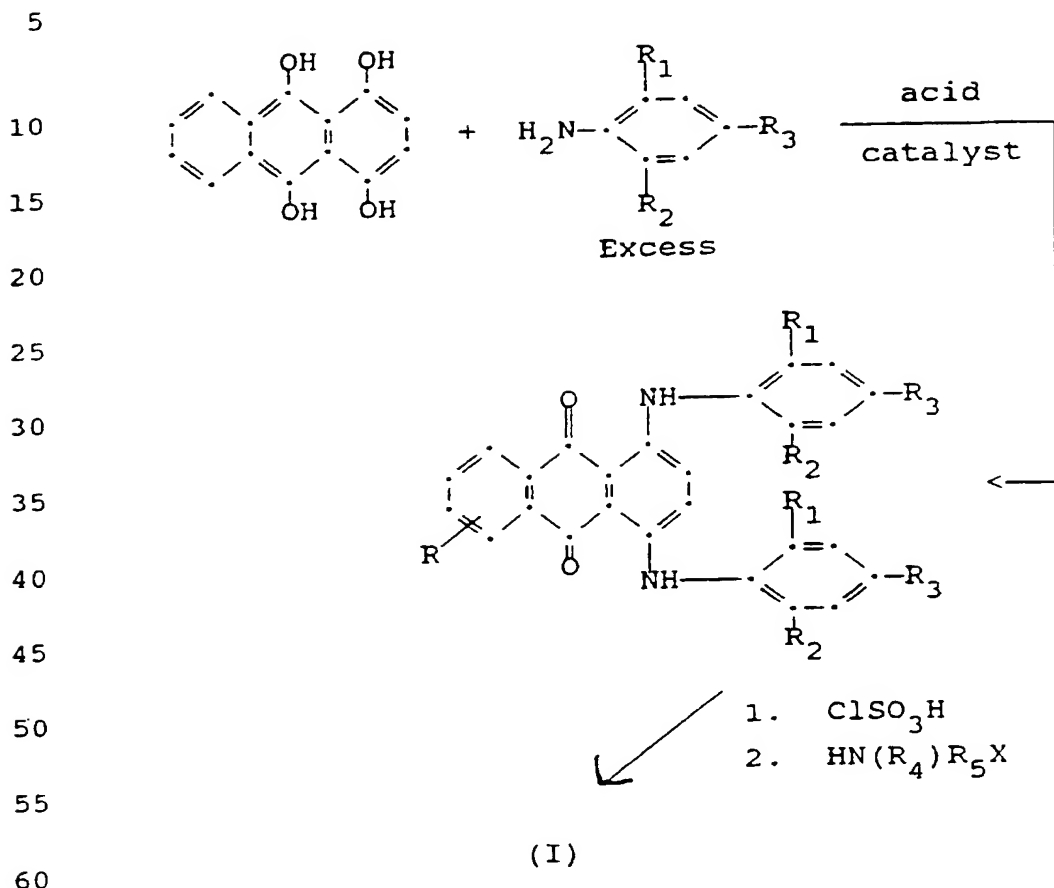
Thus, the present invention provides a polyester suitable for molding, extrusion, packaging, and fibers having copolymerized therein a blue
15 1,4-bis(2,6-dialkylanilino) anthraquinone compounds of Formula (I) plus a red anthraquinone or anthrapyridone compounds of formula (II) - (X) above. Preferred are blends having at least one blue 1,4-bis(2,6-dialkyl-anilino) anthraquinone compound of formula (I), along
20 with a red anthraquinone or anthrapyridone compound of formulae (II) - (X) above. The composition may be a neat blend of the red and blue compounds or the composition may be pre-dissolved in one of the polyester's monomeric species, e.g., ethylene glycol.

25 The total amount of toner components added depends, of course, on the amount of inherent yellow color in the polyester. Generally, a maximum concentration of about 10 ppm of combined toner components and a minimum concentration of about 0.5 ppm are required with about
30 1 - 7 ppm of blue component (I) in combination with about 0.5 - 3 ppm of red components of formulae (II - X) being preferred.

In a preferred embodiment of the present invention, the blue anthraquinone compound corresponds to structure
35 (I) above, wherein R is hydrogen; R_1 and R_2 are independently selected from methyl and ethyl; R_3 is hydrogen, methyl, or bromo; R_4 is hydrogen, C_1 - C_4 -alkyl or aryl; R_5 is selected from the group consisting of C_1 - C_6 -alkylene, C_1 - C_4 -alkylene- O - C_1 - C_4 -alkylene,
40 $-\text{CH}_2\text{C}_6\text{H}_{10}\text{CH}_2-$, arylene, or $-\text{CH}_2$ -arylene- and the red component corresponds to formula (V), wherein R_7 is

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Patent No. 3,918,976, incorporated herein by reference
and as follows:



The 1,4-bis(2,6-dialkylanilino)anthraquinone
compounds thus produced are readily functionalized if
needed by first chlorosulfonating with chlorosulfonic
acid to produce di-sulfonyl chlorides which can be
reacted with amines containing polyester reactive
groups, the general method being disclosed in U.S.
Patent No. 2,731,476, incorporated herein by reference.

Typical amines corresponding to formula $\text{HN}(\text{R}_4)\text{R}_5\text{X}$
include 2-aminoethanol, 2,2-iminodiethanol, 1-amino-2,3-
propandiol, 2-methylaminoethanol, 2-ethylaminoethanol,

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compounds further reacted with α -hydroxycarboxylic acid or derivatives thereof and/or α,β -dicarboxylic acid or derivatives thereof.

Examples of antimony compounds useful in the context of the invention include, but are not limited to the following: tributyl antimony oxide, $\text{KSb}(\text{OH})_6$, NH_4SbF_6 and SbS_3 , antimonate esters of inorganic acids, cyclic alkyl antimonate esters and aryl antimonate acid compounds such as potassium antimony, antimony oxide, antimony trioxide, antimony alkoxide, such as antimony isopropoxide, antimony halide, such as antimony chloride, antimony bromide, and antimony fluoride, antimony sulfide, sodium or potassium antimonate, antimony carboxylate such as antimony acetate, antimony glycolate and the like.

Examples of preferred antimony compounds are: antimony carboxylate, especially antimony triacetate, antimony oxide, antimony trioxide, antimony glycolate (either formed separately or during polymerization), and the like. The antimony compound desirably is added to the condensation stage or step of the polymerization.

Examples of α -hydroxycarboxylic acids which are reacted with antimony compounds to form products which are not included within the scope of the invention are ones containing 2 to 30 carbon atoms.

For example, glycolic acid, lactic acid, α -hydroxystearic acid and α -hydroxyisobutyric acid. But, those which have either a total of at least three hydroxyl and carboxyl groups or at least one aromatic ring in the α -position in relation to the carboxyl group, are particularly preferred in the present invention. Preferable α -hydroxycarboxylic acids include, for example, malic acid, α -methylnmalic acid, citric acid, tartaric acid, α -methyln tartaric acid, α -hydroxy- α' -methylnsuccinic acid, α -hydroxyglutaric acid,

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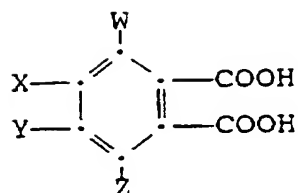
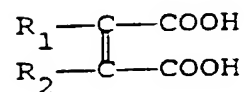
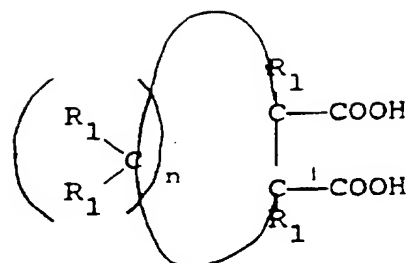
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80 wherein R_1 , R_2 , R_3 , and R_4 are identical with or
 different from each other and selected from a hydrogen
 atom and unsubstituted or substituted alkyl, cycloalkyl,
 aryl, aralkyl, allyl and alkoxy groups, said
 substituted groups having a substituent selected from
 85 carbonyl group, halogen and carboxyl groups; W, X, Y and
 Z are identical with or different from each other and

- 25 -

Such additives are generally present at 0.1 to about 20 weight % based on the total weight of said polyester composition.

Useful flame retardants, include, but are not limited to, brominated polystyrene combined with sodium antimonate.

Examples of reinforcing agents used in combination with the polyesters of its invention include are glass fibers, carbon fibers, mica, clay, talc, wollastonite, and calcium carbonate. A particularly preferred reinforcing agent is glass fiber. It is preferable that the glass fibers be present in the polyester composition at from 0.1 to 40 %, preferably 0.1 to 30 %, by weight based on the total weight of said polyester composition.

Glass fibers suitable for use in compositions containing the polyesters of the invention may be in the form of glass filaments, threads, fibers, or whiskers; etc., and may vary in length from about 1/8 inch to about 2 inches. Chopped glass strands having a length of about 1/8 inch to about 1/4 inch are preferred. Such glass fibers are well known in the art. Of course, the size of these glass fibers may be greatly diminished depending on the blending means employed, even to lengths of 300 to 700 microns or lower.

The polyester compositions of the invention may be reinforced with a mixture of glass and other reinforcing agents as described above, such as mica or talc, and/or with other additives.

This invention can be further illustrated by the following examples of preferred embodiments thereof, although it will be understood that these examples are included merely for purposes of illustration and are not intended to limit the scope of the invention unless otherwise specifically indicated. The starting

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Inherent viscosity was measured to evaluate molecular weight and was determined at 25°C using 0.5 gram of polymer per 100 mL of a solvent composed of 60 wt% phenol and 40 wt% tetrachloroethane.

5 The color values L*, a* and b* were determined using a Hunter Lab Ultrascan Spectra Colorimeter manufactured by Hunter Associates Lab Inc., Reston, VA. The colors determinations were taken at random locations on the sample and averaged. They were determined by the
10 L*a*b* color system of the CIE (International Commission on Illumination) (translated).

 The thermal stability is assessed by an evaluation of the degradation rate constant (K_d) as evaluated by monitoring the melt viscosity in air at 285°C for
15 polyethylene terephthalate and 270°C for the copolyester used in a capillary rheometer by the method described by J. Devaux et al in *Makromol. Chem.* 179, 2201, 2209 (1978). With this convention, the smaller the K_d , the more thermally stable the material is. Calculations are
20 conventional as known by those skilled in the art.

 By "thermally stable", it is meant that the K_d is lower for the polyesters of this invention when compared to polyesters of the same composition prepared by most known catalyst systems where stabilizers are not
25 employed. K_d is defined by the equation:

$$30 \quad \frac{1}{\eta} = \frac{1}{\eta_0} + K_d t$$

35 η = Melt viscosity at time t (dynes·sec)

40 η_0 = Melt viscosity at time t = 0 (dynes·sec)

45 a = Constant [0.294]

50 K_d = Thermal degradation constant

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acetate as a catalyst, has slightly lower I.V., but good color and a low degradation rate constant of 1.10×10^{-4} as measured at 270°C, despite the fact that no stabilizer was utilized. Example 7 shows the essentially the same polymer as 6, but with toner dyes added to improve the color as indicated by both the a* and b* values reported in Table 2. Example 8 is also essentially identical to 6, but this time a phosphorus stabilizer was added. As seen from the results in Table 2, Example 8 has essentially identical properties as 6 indicating that the phosphorus stabilizer is not needed.

These results show conclusively that when antimony acetate is used as a catalyst the phosphorus stabilizer is not necessary to provide thermal stability or low color. Furthermore if antimony acetate is utilized as a catalyst in conjunction with a nonreactive organic bluing agent a thermally stable polyester with excellent color is achievable.

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BT = Blue Dye having the following structure:

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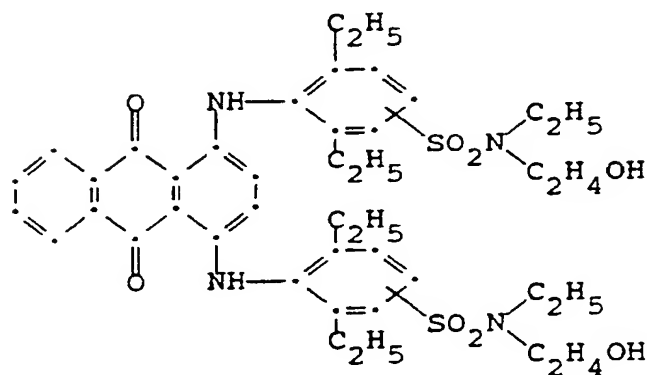
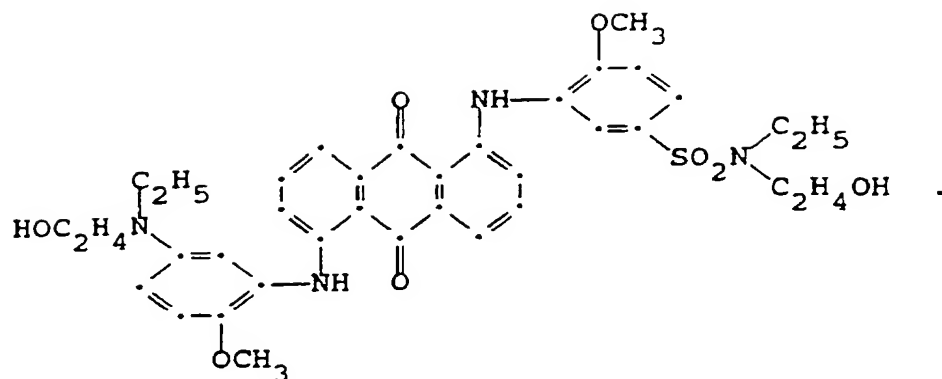
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CLAIMS

We claim:

1. A thermally stable polyester, comprising:
a polyester resin prepared by adding a dicarboxylic
acid to a glycol compound, said dicarboxylic acid
selected from the group consisting of aliphatic
dicarboxylic acids having a total of from 3 to 16
carbon atoms, alicyclic dicarboxylic acids having
to 12 carbon atoms, aromatic dicarboxylic acids
containing a total of from 8 to 16 carbon atoms,
and combinations thereof, and wherein said glycol
is selected from the group consisting of glycols
having from 2 to 12 carbon atoms, glycol ethers
having from 4 to 12 carbon atoms, and combinations
thereof,
said polyester resin having been prepared in
the presence of a catalyst system consisting
essentially of one or more antimony compounds which
is not reacted with α -hydroxy carboxylic acids,
 α,β -dicarboxylic acids or derivatives thereof.
2. The polyester of Claim 1 wherein said glycols
comprise ethylene glycol, 1,4-
cyclohexanedimethanol, 1,2-propanediol, 1,3-
propanediol, 1,4-butanediol, 2,2-dimethyl-1,3-
propanediol, 1,6-hexanediol, 1,2-cyclohexanediol,
1,4-cyclohexanediol, 1,2-cyclohexanedimethanol,
1,3-cyclohexanedimethanol, 2,8-bis(hydroxymethyl)-
tricyclo-[5.2.1.0]-decane wherein Z represents 3,
4, or 5, diethylene glycol, triethylene glycol,
dipropylene glycol and tripropylene glycol.
3. The polyester of Claim 2 wherein said glycol
comprises ethylene glycol.

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based on the total mole percentages of the acids present in the polyester being 100 mole %.

- 5 12. The polyester of Claim 11 wherein said terephthalic acid is present in the amount of 75 to 100 mole % based on the total mole percentages of the acids present in the polyester being 100 mole %.
- 10 13. The polyester of Claim 12 wherein said terephthalic acid is present in the amount of 90 to 100 mole % based on the total mole percentages of the acids present in the polyester being 100 mole %.
- 15 14. The polyester of Claims 12 and 13 wherein said polyester further comprises 65 to 100 mole % ethylene glycol.
- 20 15. The polyester of Claim 1 wherein said antimony compound is a trivalent organic antimony compound.
- 25 16. The polyester of Claim 1 wherein said antimony compounds comprises tributyl antimony oxide, antimony alkoxides, $\text{KSb}(\text{OH})_6$, NH_4SbF_6 and SbS_3 , antimonate esters of inorganic acids, cyclic alkyl antimonate esters, and aryl antimononic acid compounds, antimony oxide, antimony trioxide, antimony carboxylate, antimony glycolate, antimony halide, antimony sulfide, sodium, potassium antimonate, antimony carboxylate, antimony trioxide and antimony glycolate.
- 30 17. The polyester of Claim 16 wherein said antimony compound comprises antimony carboxylate, antimony glycolate, and antimony trioxide.

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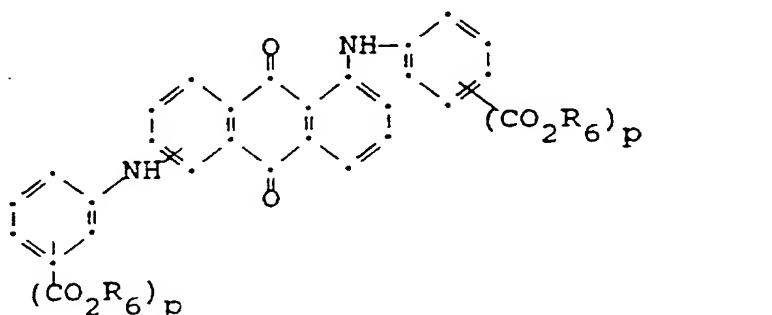
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R_5 is a linking group selected from the group consisting of C_1-C_8 -alkylene, C_1-C_6 -alkylene- Z - C_1-C_6 -alkylene, arylene- C_1-C_6 -alkylene, arylene- Z - C_1-C_6 -alkylene, C_3-C_7 -cycloalkylene, C_1-C_6 -alkylene-cyclo-alkylene- C_1-C_6 -alkylene, C_1-C_6 -alkylene-arylene- C_1-C_6 -alkylene, and C_1-C_6 -alkylene- Z -arylene- Z - C_1-C_6 -alkylene, wherein Z is selected from $-O-$, $-S-$ or SO_2 ;

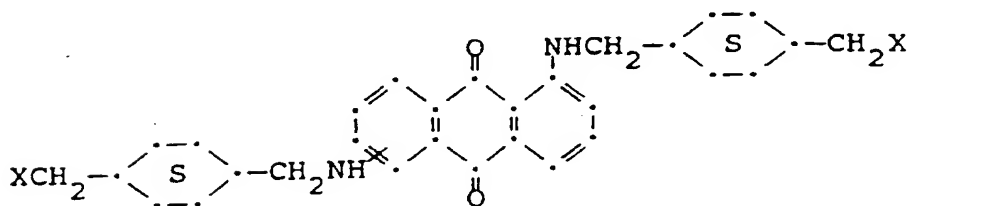
X is hydrogen or a polyester reactive group; and

m and n are independently 0 or 1; with the proviso that at least one polyester reactive group is present;

along with at least one red anthraquinone or anthrapyridone compound selected from formula (II) - (X) below:



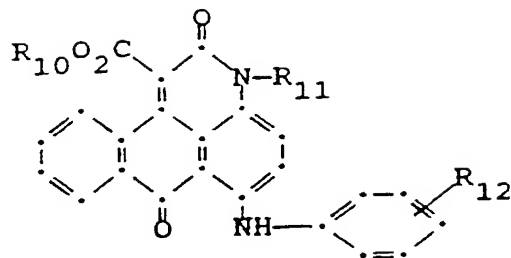
II



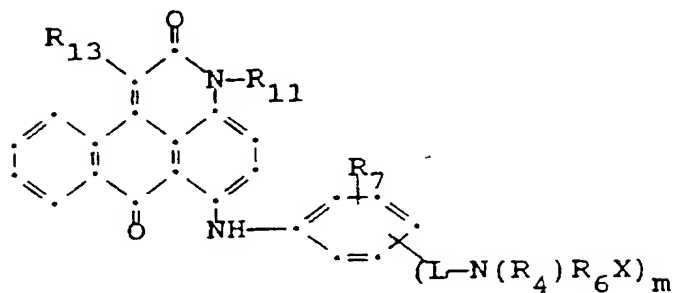
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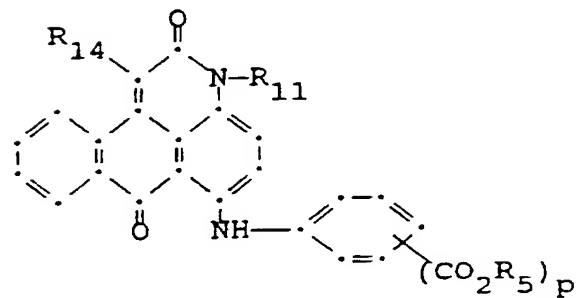
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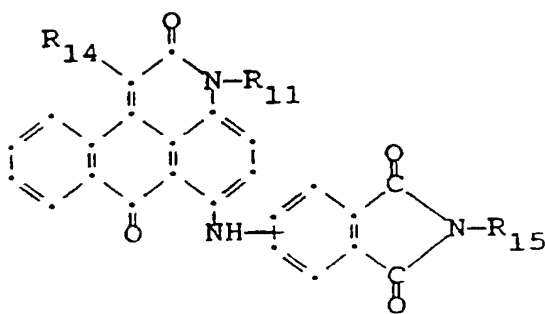
VII



VIII



IX

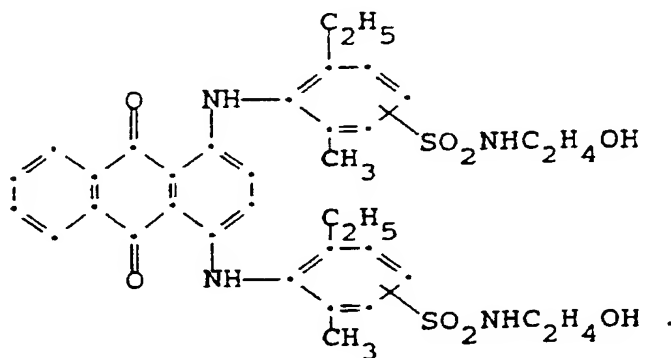


X

- 41 -

hydrogen, methyl, or bromo; R_4 is hydrogen, C_1 - C_4 -alkyl or aryl; R_5 is selected from the group consisting of C_1 - C_6 -alkylene, C_1 - C_4 -alkylene- O - C_1 - C_4 -alkylene, $-CH_2C_6H_{10}CH_2-$, arylene, or $-CH_2$ -arylene- and the red component corresponds to formula (V), wherein R_7 is C_1 - C_6 -alkoxy and R_4 and R_5 are as defined in claim 1.

21. The polyester of Claim 19, wherein the concentration of blue and red compounds taken together is from about 0.5ppm to about 10ppm.
22. The polyester of Claim 19, wherein the total concentration of blue compound(s) is about 1 to 7ppm and the concentration of red compound(s) is about 0.5 to 3ppm.
23. The polyester of Claim 19, wherein the compound of formula (I) is

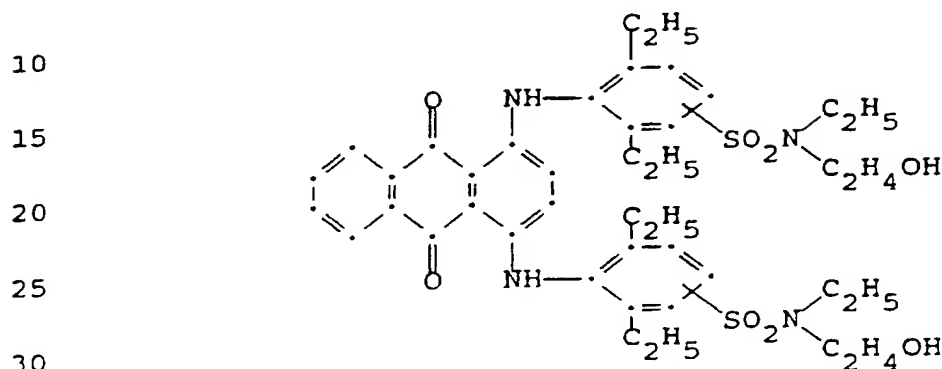


24. The polyester of Claim 19, wherein the compound of formula (I) is

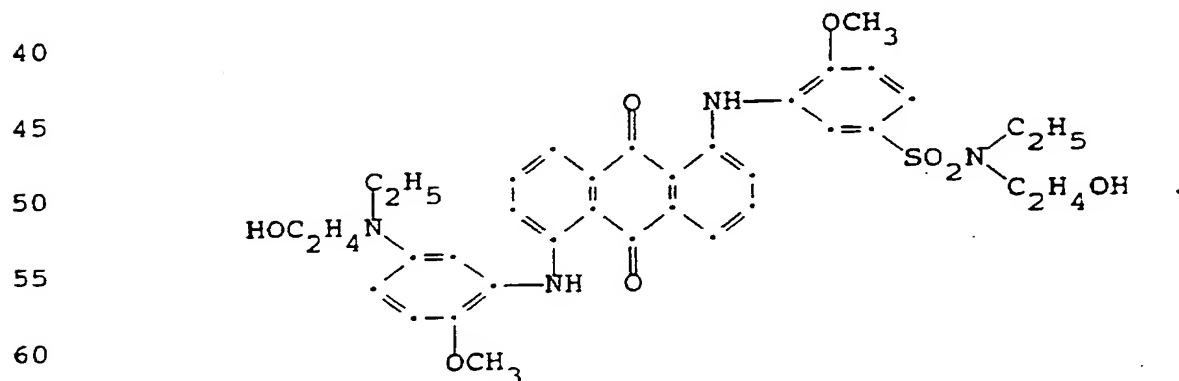
- 43 -



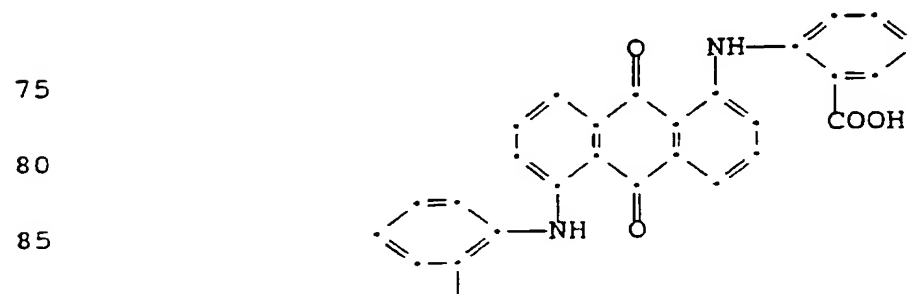
27. The polyester of Claim 19, wherein the blue compound of formula (I) is



- and wherein the red compound of formula (V) is



28. The polyester of Claim 19, wherein the red compound of formula (II) is



- 45 -

32. A process for producing a thermally stable polyester resin wherein said polyester resin is prepared by adding a dicarboxylic acid to a glycol compound,
said dicarboxylic acid being selected from the group consisting of aliphatic dicarboxylic acids having a total of from 3 to 16 carbon atoms, alicyclic dicarboxylic acids having 7 to 12 carbon atoms, aromatic dicarboxylic acids containing a total of from 8 to 16 carbon atoms, and combinations thereof, and
said glycol being selected from the group consisting of glycols having from 2 to 12 carbon atoms, glycol ethers having from 4 to 12 carbon atoms, and combinations thereof,
said polyester resin being prepared in the presence of a catalyst system consisting essentially of one or more antimony compounds which is not reacted with α -hydroxycarboxylic acids, α,β -dicarboxylic acids or derivatives thereof.
33. The process of Claim 32 wherein said glycols comprise ethylene glycol, 1,4-cyclohexanedimethanol, 1,2-propanediol, 1,3-propanediol, 1,4-butanediol, 2,2-dimethyl-1,3-propanediol, 1,6-hexanediol, 1,2-cyclohexanediol, 1,4-cyclohexanediol, 1,2-cyclohexanedimethanol, 1,3-cyclohexanedimethanol, 2,8-bis(hydroxymethyl)-tricyclo-[5.2.1.0]-decane wherein 2 represents 3, 4, or 5, diethylene glycol, triethylene glycol, dipropylene glycol and tripropylene glycol.

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42. The process of Claim 41 wherein said terephthalic acid is present in the amount of at least 50 mole % based on the total mole percentages of the acids present in said polyester being 100 mole %.
- 5 43. The process of Claim 42 wherein said terephthalic acid is present in the amount of 75 to 100 mole % based on the total mole percentages of the acids present in said polyester being 100 mole %.
- 10 44. The process of Claim 43 wherein said terephthalic acid is present in the amount of 90 to 100 mole % based on the total mole percentages of the acids present in said polyester being 100 mole %.
- 15 45. The process of Claims 43 and 44 wherein said polyester further comprises 65 to 100 mole % ethylene glycol.
- 20 46. The polyester of Claim 32 wherein said antimony compound is a trivalent organic antimony compound.
- 25 47. The polyester of Claim 32 wherein said antimony compounds comprises tributyl antimony oxide, $\text{KSb}(\text{OH})_6$, NH_4SbF_6 and SbS_3 , antimonate esters of inorganic acids, cyclic alkyl antimonate esters, and aryl antimonate acid compounds, antimony oxide, antimony trioxide, antimony carboxylate, antimony glycolate, antimony halide, antimony sulfide, sodium, potassium antimonate, antimony carboxylate, 30 antimony trioxide and antimony glycolate.
- 35 48. The polyester of Claim 47 wherein said antimony compound comprises antimony carboxylate, antimony glycolate, and antimony trioxide.

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R_5 is a linking group selected from the group consisting of C_1 - C_8 -alkylene, C_1 - C_6 -alkylene- Z - C_1 - C_6 -alkylene, arylene- C_1 - C_6 -alkylene, arylene- Z - C_1 - C_6 -alkylene, C_3 - C_7 -cycloalkylene, C_1 - C_6 -alkylene-cyclo-
 5 alkylene- C_1 - C_6 -alkylene, C_1 - C_6 -alkylene-arylene- C_1 - C_6 -alkylene, and C_1 - C_6 -alkylene- Z -arylene- Z - C_1 - C_6 -alkylene, wherein Z is selected from $-O-$, $-S-$ or SO_2 ;

X is hydrogen or a polyester reactive group; and

10 m and n are independently 0 or 1; with the proviso that at least one polyester reactive group is present;

along with at least one red anthraquinone or anthrapyridone compound selected from formula (II) - (X) below:

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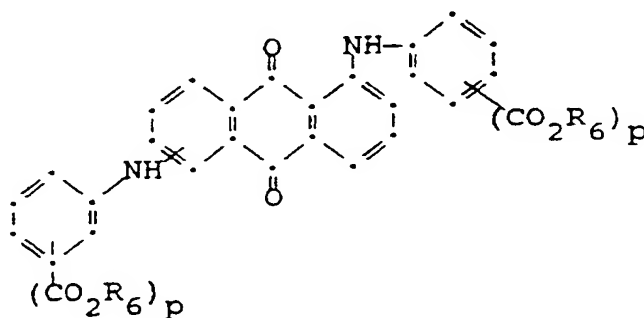
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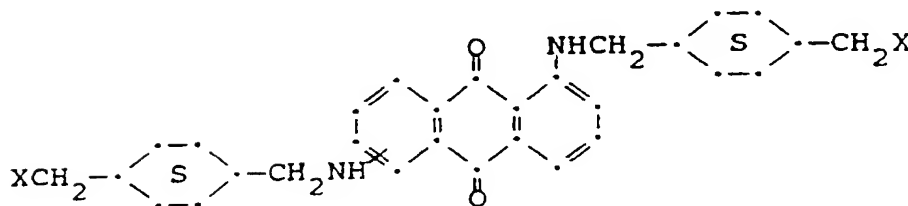
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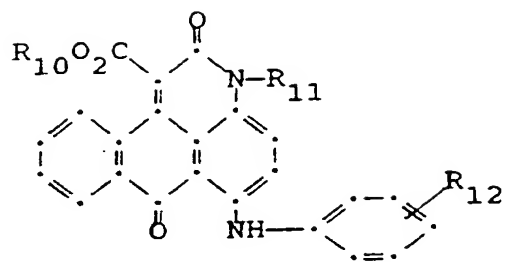


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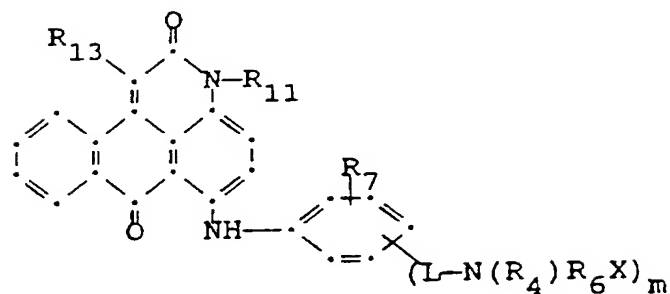


III

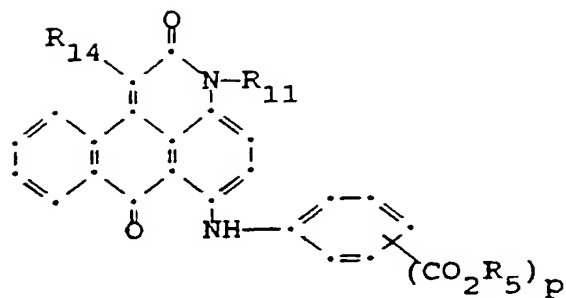
- 51 -



VII



VIII



IX

; and

- 53 -

L is -CO- or -SO₂-; X is as previously defined; m is 0 or 1; and p is 1 or 2; with the provisos that R₁₃ is hydrogen when m is 0 and at least one polyester reactive group is present.

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51. The process of Claim 49, wherein the blue anthraquinone compound(s) corresponds to structure (I) above, wherein R is hydrogen; R₁ and R₂ are independently selected from methyl and ethyl; R₃ is hydrogen, methyl, or bromo; R₄ is hydrogen, C₁-C₄-alkyl or aryl; R₅ is selected from the group consisting of C₁-C₆-alkylene, C₁-C₄-alkylene-O-C₁-C₄-alkylene, -CH₂C₆H₁₀CH₂-, arylene, or -CH₂-arylene- and the red component corresponds to formulae (V), wherein R₇ is C₁-C₆-alkoxy and R₄ and R₅ are as defined in Claim 1.

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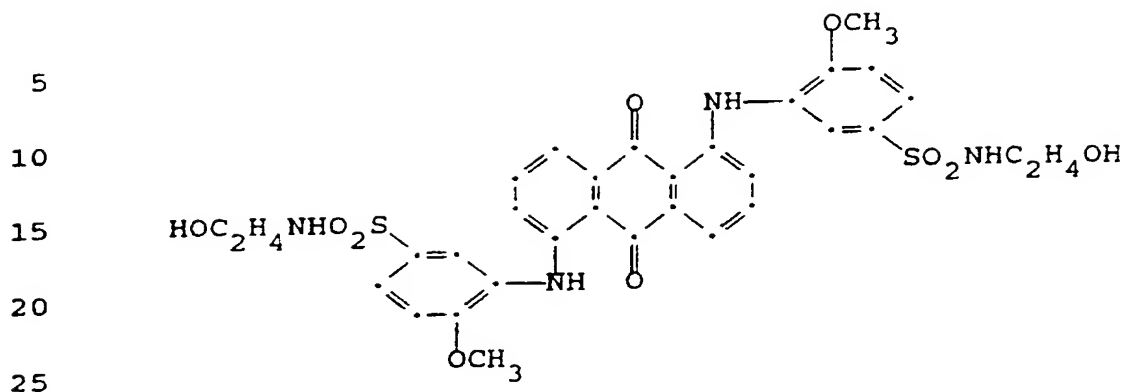
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52. The process of Claim 50, wherein the concentration of blue and red compounds taken together is from about 0.5ppm to about 10ppm.

53. The process of Claim 50, wherein the total concentration of blue compound(s) is about 1 to 7ppm and the concentration of red compound(s) is about 0.5 to 3ppm.

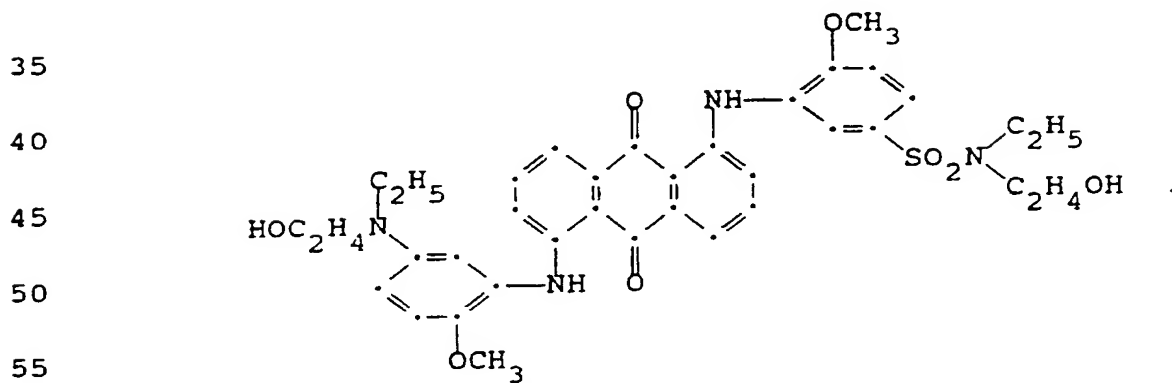
54. The process of Claim 50, wherein the compound of formula (I) is

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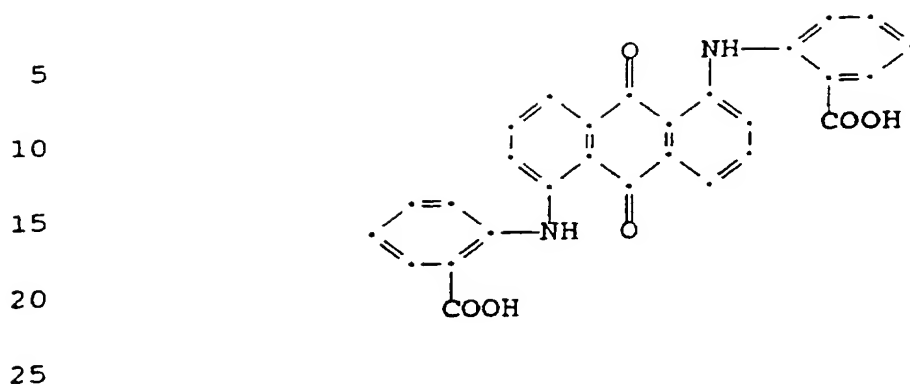
57. The process of Claim 50, wherein the red compound
of formula (V) is

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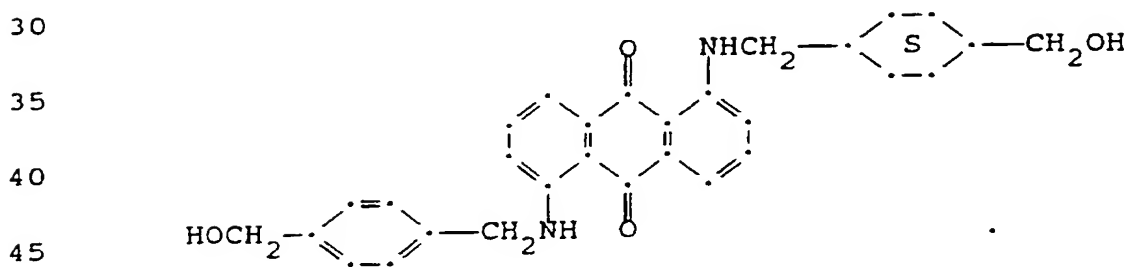


58. The process of Claim 50, wherein the blue compound
of formula (I) is

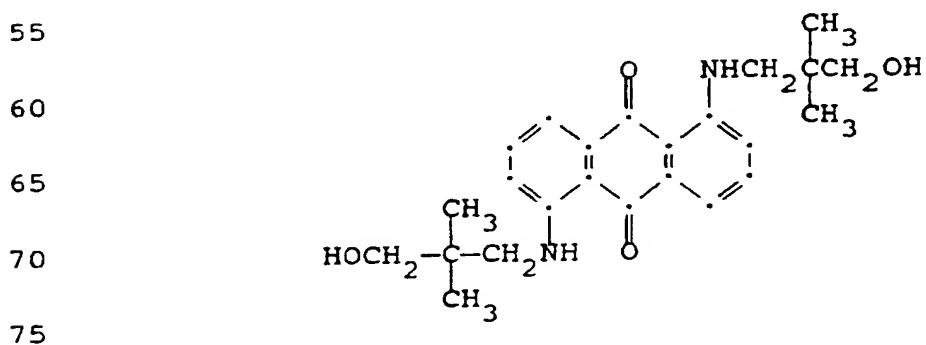
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60. The process of Claim 50, wherein the red compound of formula (III) is



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61. The process of Claim 50, wherein the red compound of formula (VI) is



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62. The process of Claim 50, wherein the red compound of formula (VIII) is

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 96/17887A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08G63/86 C08G63/685

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C08G D01F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3 705 133 A (STANLEY ET AL.) 5 December 1972	1-17, 32-48
Y	see claims 1-17	18-31, 49-62
Y	--- US 5 372 864 A (WEAVER ET AL.) 13 December 1994 see claims 1-15	18-31, 49-62
X	--- US 3 714 126 A (REID) 30 January 1973 see claims 1-10; example 1B	1-17, 32-48
X	--- US 3 935 170 A (LOEFFLER) 27 January 1976 see the whole document --- -/--	1-17, 32-48

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Date of the actual completion of the international search

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PC1/US 96/17887

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